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A. Alfano (ERC); K. Christe (ERC), "Singlet Delta Oxygen Production from a Gas-Solid Reaction"**Publication in Science**
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Singlet Delta Oxygen Production From a Gas-Solid Reaction

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Spontaneous reactions between solid alkali metal or alkaline earth peroxides and hydrogen (deuterium) halide gases demonstrate the efficient production of singlet delta oxygen in a non-liquid medium. These reactions occur under ambient conditions without the need for any external energy source. The production of singlet delta oxygen was verified by direct emission spectroscopy at 1.27 microns with a calibrated optical multi-channel analyzer. These reactions overcome the severe quenching problems encountered in liquid-phase reactions and the dangers involved in the use of potentially hazardous starting materials, such as basic hydrogen peroxide.

The long and interesting history of singlet delta (${}^1\Delta_g$) oxygen, including its discovery, study, understanding, and applications, has been described in several publications (1-4). The singlet delta state is the lowest lying excited electronic state of oxygen and it differs from the triplet ground state, ${}^3\Sigma_g^-$, in spin multiplicity. The generation of ${}^1\Delta_g$ O₂ from ground state ${}^3\Sigma_g^-$ O₂, using direct electronic excitation, is spin forbidden and inherently inefficient (5). Therefore, either complex chemical reactions, that produce

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intermediates capable of spontaneously eliminating electronically excited O₂, or compounds, that can decompose directly to produce excited state oxygen, have been studied for $^1\Delta_g$ O₂ production. Typical examples include: hydrogen peroxide with aqueous hypochlorite (6), basic hydrogen peroxide (BHP) with molecular halogens or phenols (7), the superoxide anion with water (4,8), ozone with organic substrates such as triaryl phosphites (9), alkaline peroxyacids (7,10), organic peroxides (11), and transition metal oxygen complexes (12). Although some of these reactions efficiently generate $^1\Delta_g$ O₂, they are all carried out in liquid-phase systems that cause quenching of the excited oxygen. The required rapid extraction of the gaseous singlet delta oxygen is very difficult. Furthermore, molecules capable of spontaneous elimination of electronically excited oxygen are thermodynamically unstable and, therefore, can present serious handling problems. Similar arguments may also apply to some of the precursors, such as the basic hydrogen peroxide in the BHP/Cl₂ system (13). In view of the significance of an efficient and safe $^1\Delta_g$ O₂ generator for the chemical oxygen iodine laser (COIL) (14) and other chemical and biochemical applications (1,4), the development of new methods that can overcome these problems is of great importance.

In this paper, we describe chemical reactions that spontaneously and efficiently produce singlet delta oxygen from solid alkali metal or alkaline earth peroxides and dry hydrogen- or deuterium-halide gases at room temperature. The reactions do not require external energy sources, such as heat, light, or electricity (discharge), and they avoid liquid-phase quenching and dangerous reagents.

The apparatus for generating and monitoring O₂ $^1\Delta_g$ from solid peroxides and gaseous hydrogen(deuterium) halides is depicted in Figure 1. The reaction/observation cell consisted of a 5 mm i.d. Pyrex glass tube that was attached to a 5 mm "O"-ring seal

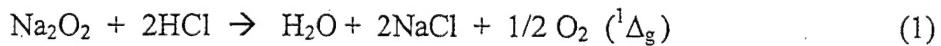
joint and a perpendicular sidearm. Opposite from the sidearm, the diameter of the tube was increased to provide a repository for the solid peroxide samples. A sodium chloride or an S-1 UV quartz window was clamped to the "O"-ring joint, and the whole assembly was placed 3 cm in front of an optical multi-channel analyzer (OMA)-spectrograph combination with the optical window facing the entrance slit. No collection optics were used.

In a typical experiment, 400 mg of a solid alkai metal or alkaline earth peroxide was added to the cell within the dry nitrogen atmosphere of a glove box. The cell was installed into the test apparatus, evacuated, and dry hydrogen(deuterium) halide gas was added through the sidearm up to a maximum total pressure of 760 torr. The OMA was kept at 160 K and an uninterrupted sequence of ten emission spectra (120 seconds collection time each) was recorded. Background subtraction was performed on all data. Several combinations of solid peroxide and gaseous hydrogen halide were tested: sodium peroxide- hydrogen(deuterium) chloride, sodium peroxide-hydrogen(deuterium) bromide, sodium peroxide-hydrogen iodide, barium peroxide-hydrogen chloride, barium peroxide-hydrogen bromide, and lithium peroxide-hydrogen chloride.

The O_2 $^1\Delta_g$ generation was monitored by the emission from its $A \rightarrow X$ ($^1\Delta_g \rightarrow ^3\Sigma_g^-$) spin-forbidden transition at 1.27 microns using a 0.3 meter Czerny-Turner spectrograph with a 600 groove/mm grating blazed at 1 micron and a near-IR sensitive optical multi-channel analyzer (OMA). The emission was identical in wavelength and contour to those produced by either a microwave discharge of an oxygen-helium mixture (15) or a BHP-chlorine sparger (16) (see upper and middle traces, respectively, in Figure 2).

All the above listed combinations of peroxide and gaseous hydrogen halide produced readily observable $O_2^1\Delta_g$ emissions, except when hydrogen iodide was used. The bottom trace in Figure 2 shows the results obtained from sodium peroxide and 580 torr of hydrogen chloride. The data represent a 120 second OMA exposure. Singlet delta oxygen emission from the Na_2O_2/HCl reaction was recorded for ten consecutive two minute exposures under three different reaction pressure conditions. The reaction cell pressure was either maintained constant by repeated addition of HCl, allowed to fall as HCl was consumed, or increased by continuous addition of HCl. In the later case, the emission increased logarithmically with pressure. Constant or decreasing cell pressures resulted in exponentially decreasing emission signals over a twenty minute period. At a constant cell pressure of 450 torr, the observed decay of the excited state emission over a twenty minute observation period was four orders of magnitude slower than that predicted from the known quenching rates of HCl and water vapor (18,19). These results demonstrate that the loss of emission due to quenching is largely offset by the continuous production of $O_2^1\Delta_g$.

The stoichiometry of the sodium peroxide/HCl reaction was experimentally established by quantitatively analyzing the material balance on a vacuum line. The results are in excellent agreement with Equation (1):

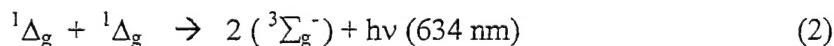


Equation (1) is also consistent with the condensation of a clear liquid on the cell walls, the conversion of the yellow peroxide starting material to a white solid (NaCl), and a decrease in pressure as the emission data were recorded.

In Figure 2, the $O_2^1\Delta_g$ emission signals from the microwave discharge, the BHP sparger, and the Na_2O_2/HCl system are compared. The discharge was operated with a

flow rate of 1×10^{-5} mole of O₂/sec plus helium, and the sparger could produce a maximum of 1.2×10^{-4} mole of O₂/sec, assuming 100% chlorine utilization. A single sample of 5×10^{-3} mole of sodium peroxide was recharged ten times with 500 to 700 torr of HCl and produced O₂ $^1\Delta_g$ emission for a total of 200 minutes. Although a quantitative comparison of these three O₂ $^1\Delta_g$ production methods is difficult due to the differences in exposure times, observation geometries, and signal durations, the gas-solid reaction must be considered a highly efficient source of excited oxygen based upon the duration and strength of the emission signal in nearly one atmosphere of a quenching gas.

An additional experiment was conducted with the sodium peroxide/hydrogen chloride pair to check for potential emission at 634 nm from the energy-pooling reaction:



At sufficiently high O₂ $^1\Delta_g$ concentrations, this energy-pooling process is known to produce a visible red glow (20). In our study, a separate OMA system sensitive in this region was used, but no evidence for this transition was found, possibly due to the dilution imparted by the high HCl pressure.

The other gas-solid reaction systems were tested in a larger cell that consisted of a 10 mm "O" ring seal joint connected to a seven inch length of 1/2 inch o.d. Pyrex tubing with 1/4 inch o.d. sidearms for gas inlet and evacuation. Larger amounts of sample were spread over a longer reaction zone, thus increasing the gas-solid contact time over that allowed by the cell of Figure 1. The listed reagent pairs were tested in a qualitative fashion. Typically, a one gram sample of solid peroxide was slowly pressurized with the hydrogen- or deuterium-halide gas to 300 to 400 torr. The gas was allowed to flow into

the cell during the measurement so that the net pressure rose during the recording of the emission data. The emission from the sodium peroxide-hydrogen bromide system was especially strong and OMA saturation was experienced at 120 sec exposure times. The results from these tests are summarized in Table 1. The emission signal intensities varied somewhat from experiment to experiment. This was partially due to small changes in the positioning of the sample cell after cleaning and reloading with fresh solid peroxide. The reactions with the deuterated halides are of special interest since deuterated compounds are significantly weaker quenchers than their hydrogen containing counterparts (21).

Table 1. Solid peroxides and gaseous hydrogen halides yielding singlet delta oxygen.

Peroxide	Hydrogen halide	Qualitative emission strength
Na ₂ O ₂	HCl	strong
Na ₂ O ₂	DCl	strong
Na ₂ O ₂	HBr	very strong
Na ₂ O ₂	DBr	very strong
BaO ₂	HCl	medium
BaO ₂	HBr	medium
Li ₂ O ₂	HCl	strong

Other simple systems were also tested. For example, potassium superoxide, KO₂, was reacted with hydrogen chloride, and a weak emission signal due to O₂ $^1\Delta_g$ was observed. However, these systems are inferior to those involving the alkali metal and alkaline earth peroxides.

In summary, the results of this study demonstrate the feasibility of efficiently generating singlet delta oxygen from gas-solid reactants without the problems associated with liquid-phase quenching. Furthermore, the required starting materials are commercially available, moderately priced, and safe to handle.

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15. A 70 watt microwave discharge (2.45 GHz) of an oxygen-helium mixture at 5 torr

total pressure was used to record the O_2 $^1\Delta_g$ emission spectrum. At the typical flow conditions of the measurement 1×10^{-5} moles of oxygen were delivered per second. A glass wool plug was placed in the discharge tube to aid in the recombination of oxygen atoms. If the discharge, gas flow, and vacuum pumping were simultaneously stopped, the emission signal decayed within one second.

16. The BHP-chlorine sparger contained 100 mL of an aqueous mixture that was 1.1 M in NaOH and 7.5 M in H_2O_2 . It was prepared by slowly adding the NaOH to cold 85% H_2O_2 over a 30 minute period while keeping the temperature of the mixture below 273 K. The sparger was immersed into a 258 K recirculating bath, and chlorine gas was introduced at a 160 sccm flow-rate. The sparger was connected to the inlet of a gas cell that was located in front of the spectrograph. The outlet of the cell was connected to a cold trap (-77 K) and a vacuum pump that maintained the pressure in the cell at 4 torr. The addition of 6 torr of either helium or nitrogen to the sparger effluent at the gas cell entrance resulted in comparable quenching of the O_2 $^1\Delta_g$ signal. Since the known quenching coefficients for He and N₂ with O_2 $^1\Delta_g$ differ by two orders of magnitude (17), the increased quenching had to be due to a longer residence time in the liquid resulting from the increased backpressure of the added gas.

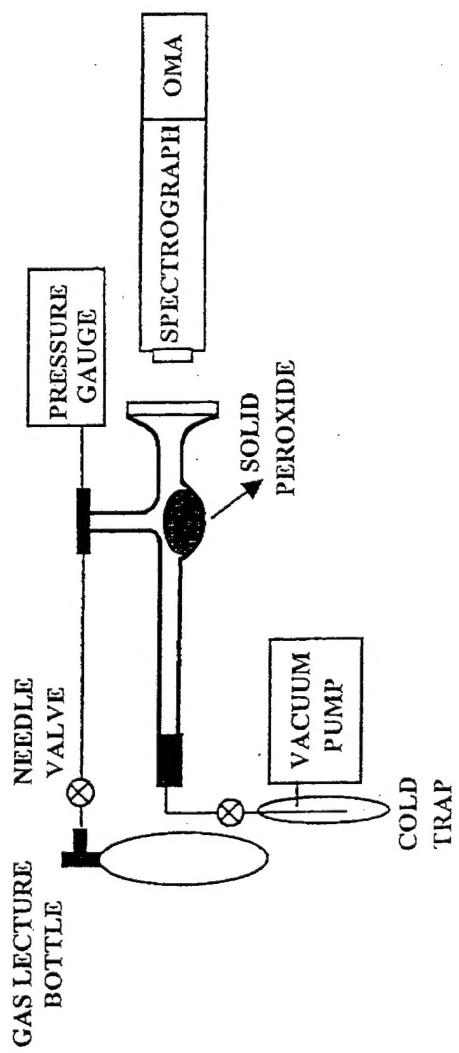
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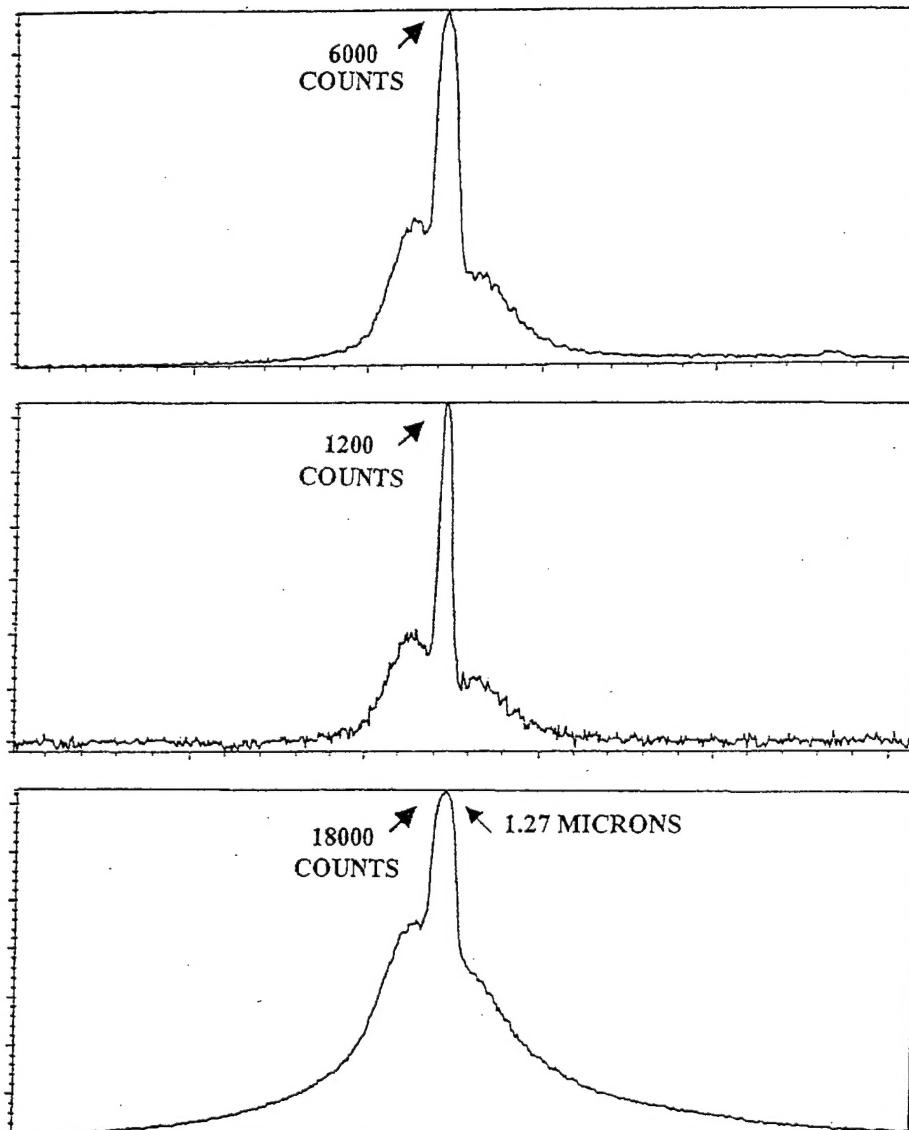
FIGURE CAPTIONS

1. Apparatus for generating singlet delta oxygen and observing its emission.
2. Emission spectra of singlet delta oxygen from a helium-oxygen microwave discharge (upper trace), a basic hydrogen peroxide-chlorine sparger (middle trace), and the $\text{Na}_2\text{O}_2/\text{HCl}$ reaction system (bottom trace), using one second exposure times for the top and middle traces, and a 120 second exposure time for the bottom trace.

FIG. 1



EMISSION INTENSITY



WAVELENGTH

FIG. 2